LOW COST HYDROGEN SENSORS FOR HYDROGEN FUEL SAFETY

Mark Daughtery, Dave Haberman, Carlton Salter
DCH Technology, Inc.
Valencia, California

David Benson
National Renewable Energy Laboratory
Golden, Colorado

Barbara Hoffheins
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Use of hydrogen as an energy carrier is increasing. Production and handling of hydrogen in industry is not new, but there are many new applications as a commercial fuel that bring its use into the public domain. Adequate safety monitoring equipment must parallel the advent of this technology. DCH Technology, in conjunction with the National Renewable Energy Laboratory (NREL) and Oak Ridge National Laboratory (ORNL), is developing and commercializing solid-state hydrogen sensors. They are designed to be inexpensive, small, and chemically inert. The NREL Fiber Optics sensor requires no electrical power at the sensing point and is ideal for high electromagnetic environments. The ORNL thick film sensor is versatile and can operate from a small battery. Data from combinations of multiple sensors can be fed into a central processing unit via fiber optics or telemetry to provide hydrogen situational awareness for small and large areas. These sensor technologies, functional attributes, and applications are presented below.

THICK FILM HYDROGEN SENSOR (TFHS)

The sensing mechanism of the ORNL sensor relies on the reversible absorption of atomic Hydrogen into and out of palladium metal in proportion to the ambient partial pressure of hydrogen gas. Changes in hydrogen concentration in the palladium matrix lead to corresponding changes in the electrical resistance of the palladium that are easily measured. The sensor consists of four palladium resistors (or legs) that are arranged in a Wheatstone bridge configuration. Figure 1 depicts the sensor and its schematic representation. The current prototype sensor chip is 2.5 cm x 2.5 cm x 0.06 cm. Two of the legs serve as reference resistors and are passivated with a thick-film resistor encapsulant to prevent entrance of hydrogen into the underlying palladium layer; thus, changes in the resistance of the palladium caused by temperature variation are compensated.

The sensor concept was successfully demonstrated using prototypes fabricated with thin film techniques. Then the sensor was designed for thick film fabrication for a variety of reasons. Effective passivations, difficult to achieve with thin films, can be made more impermeable using glass-based, thick-film compositions. Glass frit, an important component of most thick-film compositions, is formulated to provide maximum adhesion, chemical resistance, and stability over a wide range of operating conditions. A thick-film sensor is also inherently simpler, more rugged, and much less expensive to manufacture in quantity. These ideas were incorporated in the hydrogen sensor designs patented in 1994 (Lauf 1994) and 1995 (Hoffheins 1995). The palladium resistor material used in fabricating sensor samples was developed and patented by DuPont Electronics (Felten 1994).

Theoretically, the diffusion of hydrogen into a thin layer of palladium occurs on the order of milliseconds. In laboratory tests, however, the time constant of the test setup can prevent direct observation of the actual response time of the sensor. Figure 2 shows the response of a sensor to increasing concentrations of hydrogen from 0 to 2% in air. The sensor was placed in a small test chamber (50 cm^3). Hydrogen was added to air in 0.1% increments, while flow was maintained at a constant rate. Each step was 60 seconds. The sensor began to respond at the level of 0.2% H_2 in air. For each successive increment of hydrogen, sensor output increased and leveled off in 9 seconds. This time includes the time constant of the test chamber of about 2 seconds. The response in the range between 0 and 2% hydrogen is linear, so calibration is easily accomplished.

Currently the sensor is being tested to a list of specifications of interest for several commercial applications. Materials are being optimized for conditions that will typically never go above 2% H_2 in air. The temperature range is -40°C to +60°C. The sensor has been successfully tested between 20°C and 200°C [Hoffheins 1998]. In general, the response is faster at the higher temperatures, but the magnitude of the response is lower because of reduced hydrogen solubility in the palladium. An acceptable response time for the intended commercial applications is 3 seconds. The raw output from current prototypes does not meet that requirement; however, methods to use the rate of response and the dc output with external circuitry to predict the hydrogen concentration are being examined. Another very important performance objective is that the sensor is insensitive to the following compounds: CO, CO_2, CH_4, NH_3, propane, butane, and acetylene. In preliminary tests, sensors were exposed to carbon monoxide, propane, and methane. The response indicated little or no effect on the sensor. The sensor appears to be insensitive to these compounds. More tests will be conducted with the above and other compounds to verify this performance.

APPLICATIONS FOR THE TFHS

DCH Technology is commercializing the TFHS. This device is most applicable as a low cost alarm sensor. The principal applications currently being addressed are for hydrogen powered automobiles, personal safety badges, and remote area monitoring.

The safety badge application has been chosen for initial market penetration because the environmental requirements match current knowledge of the performance of the sensor. DCH has built a prototype badge that is approximately the size of a standard business card and roughly one-quarter of an inch thick. DCH is undertaking a more detailed market analysis to determine customers and distribution partners, additional functional benefits (such as activating a vibrator to signal hydrogen), specific sensor technical requirements, and cost targets. A product specification will be developed from this data and an initial product will be built and distributed for alpha testing. In parallel with the product definition effort, DCH and ORNL will complete the technical bounding of the sensor operational characteristics, including response time, cross-sensitivity, and applicable firmware.

Sensors for automotive applications are being developed now. There are three general areas of interest: Low level alarms to sense leaks from hydrogen storage and delivery lines; sensors for high concentrations of hydrogen that exist in the output of reformers or inputs to fuel cells; and medium level sensors that are needed in the exhaust stream of an internal combustion engine running on hydrogen. The sensors considered in this paper are for the low level alarm application.

The automotive requirements for the device are low cost (one to four dollars per sensing point), rapid response, rugged and repeatable operation in the automotive environment, and a unit life of ten years. In addition, there cannot be any false positives, and the size of the sensor must be small enough to fit into critical areas.

The automotive requirements are considerably more stringent that those for the safety badge. The operating temperature range is very broad, from –40°C to over 60°C. While the TFHS is thermally self compensating by design, the sensor response speed decreases with decreasing temperature and the sensitivity decreases with increasing temperature. ORNL and DCH are currently investigating the sensor response under these conditions. Software methodologies are being investigated to provide interpretive decision making based on sensor output to both speed up response speed and to activate hierarchical responses to decreasing, continuing or increasing hydrogen concentrations.

The automotive operating environment can expose a sensor to a multitude of gases and vapors. The sensor must have no cross sensitivity and not be poisoned by such chemicals. To address these requirements, DCH and ORNL are testing the sensor against other gasses, such as CO_2, CH_4, NH_3, O_2 variations, water vapor, acetylene, and chemical vapors to which the sensor could be exposed. Additional considerations under evaluation are susceptibility of the sensor and associated wiring and electronics to electromagnetic interference. Also, sensor ruggedness and durability are being characterized. Finally, after all these technical considerations are put to rest, the sensor must meet the cost goals of the automotive industry.

All of these parameters are being addressed in cooperation with major automotive manufacturers. Publicly sold fuel cell powered cars are on the horizon and the need for low cost hydrogen sensors that meet the needs of the automotive environment is now.

The final application area being addressed for the TFHS is for monitoring of large industrial areas, both indoor and outdoor, which have risks of hydrogen leakage. DCH is aware of industrial disasters that were prevented because the company involved discovered the leak using a portable sensor. DCH intends to make hydrogen sensing simple and cost effective so companies can easily install the protection they need. In particular, DCH is developing a wireless transmission capability to attach to the TFHS for remote and/or large area monitoring. A receiver unit will collect transmitted signals from multiple sensors. This unit can then be hard wired into control electronics or its output signal transmitted to remote control stations. The receiver could be one of many a large area network. DCH is presently evaluating transmitter suppliers as well as looking at making the transmitter in-house. In parallel, DCH is developing the market analysis to determine operating and cost specifications. In a few months, DCH will finalize the specifications and make the make/buy decision. This action will be followed by development of a prototype, obtaining FCC approval, and alpha testing.

FIBER OPTICS HYDROGEN SENSOR (FOHS)

The use of a fiber-optic, hydrogen-gas-leak detector has advantages of inherent safety (no electrical power in the vicinity of the sensor), reduced electromagnetic interference, lightness of weight, and low cost. Most if not all of the needed electro-optic components could be integrated into a single application-specific integrated circuit (ASIC) for economical mass production. An analysis of the probable manufacturing costs has shown that it should be possible to mass-produce similar detectors for about $5 each (not including the cost of the optical fiber).

In this design, a thin-film coating at the end of a polymer optical fiber senses the presence of hydrogen in air (Benson, et al 1998). When the coating reacts reversibly with the hydrogen, its optical properties are changed. Light from a central electro-optic control unit is projected down the optical fiber where it is reflected from the sensor coating back to central optical detectors. A change in the reflected intensity indicates the presence of hydrogen. The fiber-optic detector offers inherent safety by removing all electrical power from the sensor sites and reduces signal-processing problems by minimizing electromagnetic interference. Critical detector performance requirements include high selectivity, response speed, and durability as well as potential for low-cost production.

Preliminary experiments were conducted with simple sensors. The end of a polymer optical fiber was coated with 500-nm WO_3 and a superficial layer of 10-nm palladium. Figure 3 shows a calibration curve obtained from such a sensor in air with various concentrations of hydrogen. The reflected signal at 850 nm is attenuated by the optical absorption in the WO_3 in proportion to the reaction with hydrogen, which in turn is proportional to the hydrogen concentration. The sensitivity is adequate for detection of the hydrogen well below the lower explosion limit of 4% in air.

A self-contained, hand-held portable fiber-optic hydrogen sensor was designed and built. The light source is a high- brightness, broad-spectrum "white" (phosphor-enhanced) LED. The light from the LED is projected into the proximal end of a 1-mm-diameter polymer optical fiber and transmitted through a 1 x 2 coupler to an exit port on the instrument. The optical-fiber sensor is plugged into that port with a standard fiber-optic ST connector. Light reflected from the sensor coating on the distal end of the fiber is returned to the instrument, and half of its power is directed through one of the coupler legs to a dichroic mirror. The dichroic mirror splits the return light beam into long- and short-wavelength portions that fall separately on two different photo-diode amplifiers. The voltage signals from the two photo-diodes are divided one by the other in an analog divide circuit. Figure 4 shows a schematic illustration of the detector's design features.

APPLICATIONS FOR THE FIBER OPTIC HYDROGEN SENSOR

Initially the FOHS was developed for automotive use because it will not inject any electrical circuitry into the sensed area and the signal transmission is over the fiber, which is insensitive to electromagnetic interference. However, this sensor needs further development work to accelerate the response time, especially at the low temperatures required by the automotive specifications. In the mean time, there are two applications for which the sensor, in its current state of development, can be used. The first is as a weld quality sensor. A sensor can be attached to the weld within hours after the weld is completed and used to measure the rate of hydrogen out gassing, which indicates the concentration of dissolved hydrogen in the welded steel. Using this process, the weld condition can be read in minutes. The current methods for measuring the concentration of dissolved hydrogen in welded steel require approximately a day to read and must use witness samples. The fiber optic sensor could be used, as a secondary standard, in conjunction with the existing method. As the faster method becomes proven, standards for its use as a primary weld quality sensor could be established.

The second application is in monitoring battery rooms. Again, multiple fibers would be easily distributed throughout the room and monitored at a central location. In this application, the fiber optic approach displays its inherent advantages of multi-point sensing and installation versatility.

INTEGRATED APPLICATIONS

DCH plans to mix and match these two technologies, along with the DCH Robust Hydrogen Sensor monitor, to provide optimal situation awareness in complex hydrogen use environments. To do this cost effectively, DCH is planning to develop common electronic packages which include easily modifiable software inputs to not only tailor the sensors to the customers unique application, but moreover, to give the user the tools to modify and expand their hydrogen sensing capabilities.

SUMMARY

DCH Technology is commercializing state of the art hydrogen sensors developed by Oak Ridge National Laboratory and the National Renewable Energy Laboratory. This blend takes the scientific knowledge resident in these laboratories and creates applicable, timely, and meaningful commercial products that assist the development of the hydrogen fuel economy. These sensors are necessary to help carry this development into the public domain.

Key Words: Hydrogen, Sensors, Safety

References

Benson, D. K., C. E. Tracy, and D. S. Bechinger, 1998. "Fiber Optic Device for Sensing the Presence of a Gas. U. S. Patent No. 5,708,735.

Felten, J.J. 1994. "Palladium Thick Film Conductor." U.S. Patent No. 5,338,708.

Hoffheins, B.S. and R.J. Lauf. 1995. "Thick Film Hydrogen Sensor." U.S. Patent No. 5, 451,920.

Hoffheins, B.S., R.J. Lauf, T.E. McKnight, and R.R. Smith, 1998. "Design and Testing of Hydrogen Sensors for Industrial Applications," *Polymers in Sensors, Theory and Practice,* ACS Symposium Series 690, N. Akmal and A.M. Usmani, pp. 90-101.

Lauf, R.J., B.S. Hoffheins, and P.H. Fleming. 1994. "Thin-Film Hydrogen Sensor." U.S. Patent No. 5,367,283.

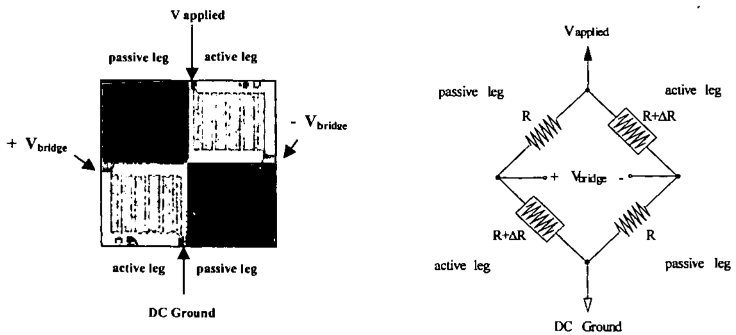

Figure 1. Thick Film Hydrogen Sensor Chip and Schematic Representation

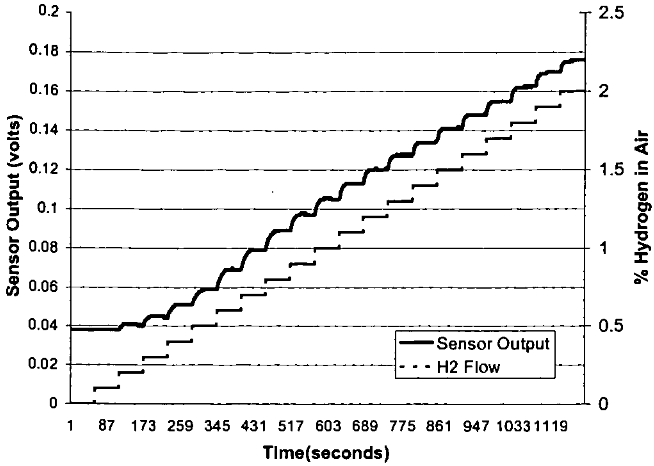

Figure 2. Sensor response to increasing concentrations of hydrogen in air

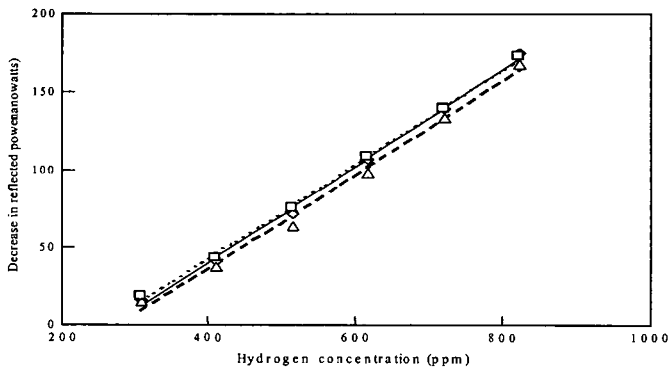

Figure 3. Calibration curves for a simple reflective WO_3/Pd-coated F-O sensor.

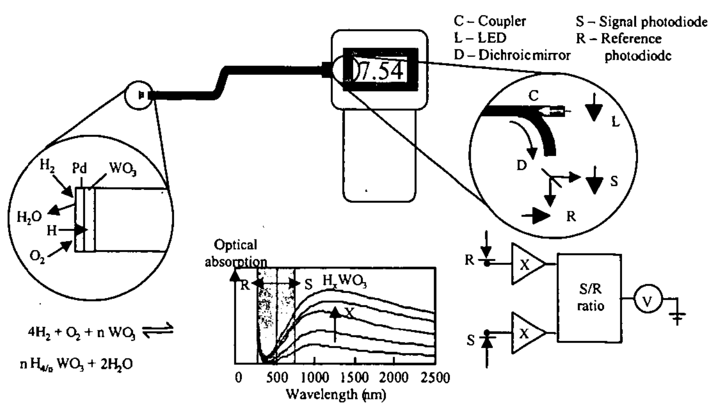

Figure 4. Schematic diagram of the prototype portable fiber-optic, hydrogen-gas-leak detector showing selected design features.